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(71) DEINKING/SOLVENT EXTRACTION TECHNOLOGIES LTD, CA
(51) Int.Cl.⁶ C10G 1/04, B03B 9/02
(54) **PROCEDE DE SEPARATION ET D'ISOLEMENT DE
GOUDRONS, D'HUILES, D'ARGILES RENFERMANT
POTENTIELLEMENT DES MINERAUX RECUPERABLES ET
SABLE PROVENANT DE SABLES ET DE SHALES
BITUMINEUX EXTRAITS**
(54) **A PROCESS FOR THE SEPARATION AND ISOLATION OF
TARS, OILS, CLAYS POTENTIALLY CONTAINING
RECOVERABLE MINERALS, AND SAND FROM MINED OIL
BEARING SANDS AND SHALES**

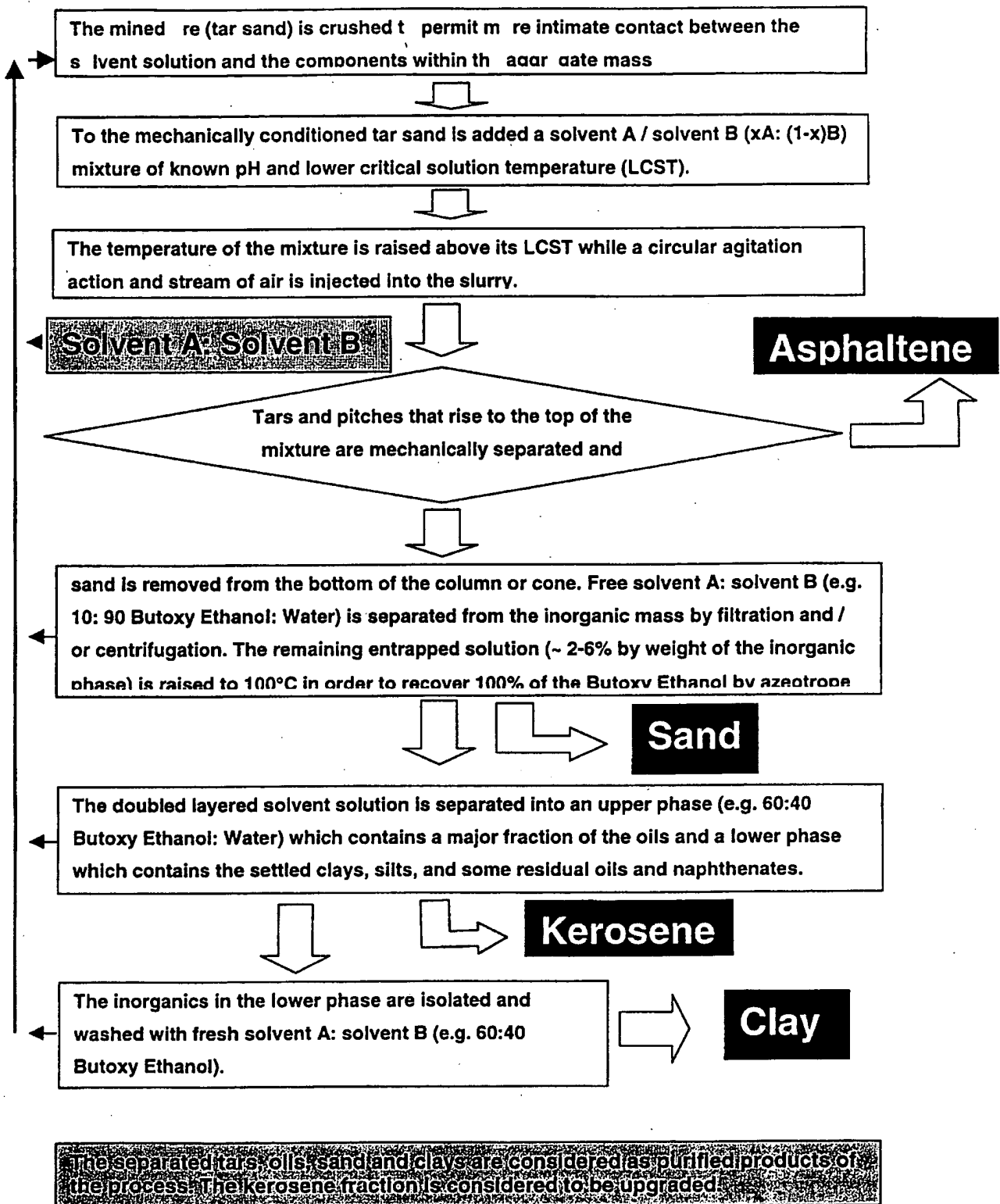
(57) A Process for the total separation and recovery of four constituents, namely 1) insoluble pitches and tars also known as asphaltenes, 2) a kerosene based oil fraction, 3) clays, shales and silts of less than 80 µm mesh which may contain harvestable precious metals and 4) sands of greater-than 80 µm mesh. Recombination of the hydrocarbon fractions is the bitumen portion of Tar Sands or Shales.



{57}ABSTRACT

A Process for the total separation and recovery of four constituents, namely 1) insoluble pitches and tars also known as asphaltenes, 2) a kerosene based oil fraction, 3) clays, shales and silts of less than 80 μm mesh which may contain harvestable precious metals and 4) sands of greater than 80 μm mesh. Recombination of the hydrocarbon fractions is the bitumen portion of Tar Sands or Shales.

Flow Chart of the Process:



Specifications / Background of the Invention

This invention relates to the separation and isolation of oil sand aggregates into four components: 1) tars and pitches, 2) a kerosene fraction, 3) clays, silts (particle sizes of less than 80 μm) and 4) sand (particle sizes of greater than 80 μm).

It is known that oil sands can be separated and oil fractions isolated by one of many processes of which the ranked highest to lowest preference is the:

- a) CHWE (Clark Hot Water Extraction Process) [1],
- b) OSLO HWE (Oslo Hot Water Extraction Process) [2],
- c) OSLO CWE (Oslo Cold Water Extraction Process) [2],
- d) AOSTRA – Takiuk Process [3],
- e) ZEFTE (Zero Fine Tailings Extraction Process) [4], and
- f) BITMIN (Counter Current Desander Process) [5].

[1] FTFC (Fine Tailings Fundamentals Consortium) "Vol 4 –29. Laboratory Experiments on the Clark Process" In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

[2] FTFC (Fine Tailings Fundamentals Consortium) "Vol 4 –9. OSLO Hot and Cold Water Extraction Processes" In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

[3] FTFC (Fine Tailings Fundamentals Consortium) "Vol 4 –6. AOSTRA – Takiuk Process" In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

[4] FTFC (Fine Tailings Fundamentals Consortium) "Vol 4 –8. Zero Fine Tailings Extraction (ZEFTE)" In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

[5] FTFC (Fine Tailings Fundamentals Consortium) "Vol 4 –8. BITMIN" In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

SOME OF THE INHERENT PROBLEMS ASSOCIATED WITH SOME OR ALL OF THE ABOVE ARE:

Energy Usage:

The processes require large net input of thermal and / or mechanical energy.[6]

[6] Strand, W. L.; Canadian Pat. 2 124 199 (1992 06 11)

Tailings and Storage Space:

They also generate large quantities of tailings and require indefinite storage space. [6]

Bitumen Yields:

Except for the AOSTRA-T Process, unacceptably low yields (54 – 92%) of bitumen are separable from the tar sands using present day technology. In fact, yields of 92 – 96% are considered to be high using the present art. [7]

[7] Sparks B.D., Majid A., Woods J.; Canadian Pat. 2 093 142 (1994 09 27)

In this invention yields of 99% are considered low from any and all of the ore bodies found in Alberta, Canada.

Hence, not only can more oil be squeezed out of less ore but utilization of the steps in our invention makes access to the lower grade ores economically viable.

Water usage:

Again, except for the AOSTRA-T Process, large volumes of water are used in the extraction of bitumen. On average 0.7 to 3 MT of water are required per Metric Ton

of ore (depending on the bitumen content of the ore). The lower the bitumen content the higher the volume of water required. Presently, in the case of the 12% bitumen content ore, 420,000 MT of water are required per day of full operation.[8]

[8] FTFC (Fine Tailings Fundamentals Consortium) "Vol. 2 – 3" In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

Environmental Concerns:

Because the spent water presently generated contains toxic naphthenates, oil residues, and fine tailings, storage and containment of the waste waters has become an integral part of the process. The presently projected required volume of settling ponds doubles every 400 days. This is expected to decrease to 300 days when the Aurora mine comes on stream in the year 2004 i.e. 460,000,000 m³ per annum of new storage space for spent water shall be required.

It has been estimated that it will take 100 – 300 years for the colloidal of the fine tailings to agglomerate to a soft clay before release of the above mentioned waters shall be permitted to the environment. " *Without further treatment of the existing fine tailings and without process modifications to reduce the rate of production of "new" fine tailings, by the year 2030, over one billion cubic meters of a non-consolidating fine tailings would exist at the bottom of these lakes.*"

...since "Containment of the entire water system with the operating process is required as part of the operating license agreement between the Provincial Government and the two commercial plants." [9, 10]

[9]] FTFC (Fine Tailings Fundamentals Consortium) "Vol. 4 –5. " In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

[10] Mac Kinnon, M. and Sethi, A.; *A Comparison of the Physical and Chemical Properties of the Tailings Ponds at the Syncrude and Suncor Oil Sands Plants, Oil Sands_ Our Petroleum future Conference, Edmonton, Alberta, April 4-7, 1993.*

AOSTRA Takiuk Process [11]

An advantage of the AT Process is that no toxic tailings are generated. Extra energy costs incurred by the process are partially offset by elimination of treatment and maintenance costs of the wastewater containment ponds. Although the process is self sufficient, the expended energy and specialty equipment must be costed against the process. Our process minimizes such cost while providing the opportunity to sell the energy to the open market.

[11] FTFC (Fine Tailings Fundamentals Consortium) "Vol. 4 -10." In: *Advances in Oil Sands Tailings Research*, Alberta Department of Energy, Oil Sands and Research Division, Publisher.

SUMMARY OF THE INVENTION

The present invention provides a process whereby trapped and bound bitumen can be removed from an inorganic agglomerate of various size particles. Upon detachment and because of the ability of the solvent to physically set up a phase mixture system which has inherent density and solubility extremes, tars can be separated from oils and sand can be separated from clays and silts.

Such solvent mixtures have the ability to separate into biphasic mixtures simply by adjusting the temperature of the solution or by changing its inorganic salt concentration.

The separating solvent solution is an aqueous mixture of lipophilic liquids that exhibit a Lower Critical Solution Temperature.

Some liquids exhibit total solubility over a range of concentrations and temperatures but partition into biphasic systems at specific concentrations and temperatures. They possess the specific ability to raise the lipophilic and hydrophilic characteristics of a solution by simple manipulation of the process variables. In other words, simple adjustment of the salt concentration or temperature greatly expands the separation abilities of the constituent solvents. An example is Butoxy Ethanol in water. Solutions of greater than 10% and less than 60% Butoxy Ethanol will, below approximately 40°C remain in solution but partition into a biphasic system above 40°C.

For example, 100 ml of totally miscible Butoxy Ethanol (density 0.934 g/ml) will, at 50°C give a biphasic system of 10 mls 60% Butoxy Ethanol in Water as a top phase (density 0.92 g/ml) and 90 mls of 10% Butoxy Ethanol in Water as a bottom phase (density 0.99 g/ml).

Such phenomena are known as Lower Critical Solution Temperatures. When the reverse phenomena is exhibited i.e. a biphasic mixture at a low temperature becomes a single phase at a higher temperature the solvents are said to have a Higher Critical Solution Temperature (HCST).

The present invention provides a method of separating the organic from the inorganic phase in tar sands with a recyclable liquid composition whose LCST is between 0°C and 100°C comprising:

Sodium silicate	0 – 2.5%
Sodium hydroxide	0 – 2.5%
Alkyl or di alkyl glycol or di glycol ether and / or	
Propyl glycol ether	Ingredient dependant
Triethyl amine and / or diethyl methyl and / or dimethyl pyridine and / or	
methyl pyridyl and / or methyl piperidene	0 – 10%
Water	to 100%

In preferred embodiments of the inventions the following proportions of components can be used.

Sodium Hydroxide and/or Sodium Silicate 0-2.5%, preferably 0.5 to 2.5, particularly preferable 1-2%

All glycol ethers 0-100%, preferably 10 to 60 particularly 15 – 25%, especially 20%.

ADVANTAGE OF OUR PROCESS OVER THE PAST ART

Some obvious advantages of the process are:

1) Simplicity of the equipment and the process	Reduction in capital costs and maintenance fees.
2) Raising the recovery rates of the hydrocarbon fraction well above 92%	Between 15 and 30,000 extra barrels per day.
3) Making the raw material source usage of the low grade ore (6- 10% Bitumen content) economically viable	Some where between 90 and 120 B\$US.
4) Facile separation of the solid hydrocarbons from their liquid counterparts	Short cycle time and therefore reduced equipment size requirements.
5) Concentration of the liquid hydrocarbon fraction by partitioning it between the two phases of the solvent mixture at temperatures just above the LCST	Lowering the process temperature to just above 40°C.
6) Generate two separate hydrocarbon streams at the mine site (Asphaltenes and liquid hydrocarbons)	Eliminate transportation of the inorganic phases.
7) Generate a solvent system which has a Freezing point of - 10°C	This is more of a pour point than a freezing point.
8) Work with non - flammable solvents i.e. flash points above 100°C	Insurance premiums should be low.
9) Reduce energy usage	Process ores just above 40°C
10) Eliminate the need for waste water Containment ponds	No toxic waste and no fine tailings.
11) Eliminate the projected volumes of toxic fine tails	Holding ponds not needed.
12) Eliminate the need for Tailings Oil Recovery	No wastewater.
13) Recycle the solvent system in a closed cycle	Recovery of the naphthenates and thio compounds.
14) Segregation of the mineral clays from the sand for further processing	Recovery of >99% pure silicon dioxide
15) Provide the opportunity to recover precious metals	

from the inorganic isolants.	
16) Extension of the process to cleaning up man made spills	

Experimental Example

- 1) To a 6-12% by weight sample of tar sand add an equivalent weight of greater than 10% by volume Butoxy Ethanol in Water. The solvent mixture may contain up to 0.75% of sodium hydroxide and *meta* sodium silicate respectively.
- 2) The mixture is stirred and a stream of air introduced while being heated above 40°C.
- 3) Heating the mixture above 40°C causes the liquid to separate into two layers or phases. The upper layer and lower layers are 60:40 and 10: 90 solutions of Butoxy Ethanol: Water respectively.
- 4) Tars and pitches (Asphaltenes) whose densities are less than 0.99 g/cc rise to the upper layer. Those which are greater than 0.92 and less than 0.99 g/cc rise to the interface between the two layers.
- 5) The asphaltenes can now be isolated by filtering those, which are suspended in the liquid, and by skimming those surfaces on which they have been deposited.
- 6) The asphaltenes are washed with fresh 60:40 BE: Water and azeotrope dried by raising their temperature to 100°C. The asphaltenes are further processed at the refinery level.
- 7) Purified sand is found at the bottom of the column or cone. It is washed with fresh 60:40 BE: Water to ensure it is bitumen free before being passed through a centrifugal thickener as is used in the paper industry. The semi dry, silt free sand is heated to 100°C in order to azeotropically recover all butoxy ethanol. The purified sand (greater than 99% SiO₂) can be used as an abrasive or by the glass industry.
- 8) The clay collects on top of the sand. Agitation and air causes the fine particles to separate from the larger sand particles.

- 9) Within the scope of our experiment we used an aspirator attached to a pasteur pipette to collect the clay. It was washed with 60:40 BE: Water in order to ensure it was bitumen free before azetropically drying it.
- 10) Depending on the source of the ore, the cleaned clays (mainly kaolinite and illite) may have commercial applications or precious metal extraction possibilities.
- 11) The kerosene fraction is found dissolved in the top layer. It is recovered by fractional distillation.
- 12) All recovered solvents and washings are recycled. They can be used "as is" in a primary extraction step or after purification by distillation.
- 13) Bitumen yields of greater than 99% are attainable.

The embodiment of the invention in which an exclusive property or privilege is claimed and defined as follows:

- 1) A process which causes the separation of bitumen that is interstitially entrapped and bound to a substrate such as sand and mineral clays in oil sands and shales.
- 2) A cleansing action consisting of treating a substrate surface and its interstitial areas with a "Solvent xA: Solvent (1-x)B" mixture which has a Lower Critical Solution Temperature (LCST).
- 3) A process as defined in claim 2 in which the solvent has a pH range from less than 1 to more than 14 but preferably between 7 and 12.
- 4) A process as defined in claim 3 in which the solvent mixture is controlled by the addition of either inorganic or organic acids and bases.
- 5) A process as defined in claim 2 in which the ionic strength and hence the LCST is controlled by the addition of salts.
- 6) A process as defined in claim 2 in which the freezing point is controlled by the ratios of the solvents in the mixture.

- 7) A process as defined in claim 2 in which injecting the solution in a counter current manner and at a temperature less than the LCST and to heat the solution as it moves through the ore body.
- 8) A process as defined in claim 7 in which the lower temperature solvent starts to remove the oils from the ore and the higher temperature solvent phase concentrates the oils.
- 9) A process as defined in claim 2 in which the LCST is between 0 and 100°C.
- 10) A process as defined in claim 2 in which the ore moving in a downward direction and the liquid in reverse direction (i.e. counter current) so that introduction of air within the ore mass further urges the lower density asphaltenes, to rise towards the top of the mixing chamber.
- 11) A process as defined in claim 2 in which the ore moving in a downward direction and the liquid in reverse direction (i.e. counter current) so that introduction of air within the ore mass further urges the smaller sized particles to rise towards the top of the mixing chamber.
- 12) A process as defined in claim 2 in which the ore moving in a downward direction and the liquid in reverse direction (i.e. counter current) so that introduction of air within the ore mass further urges the upper phase liquid to rise towards the top of the mixing chamber.
- 13) A process as defined in claim 2 in which the solid ore gradually distributes itself into "sized particle layers" of clay silt and sand that can be shunted to further refining processes.
- 14) A process as defined in claim 2 in which the column of liquid is comprised of an upper layer of lower density that contains the major portion of the oils and a lower layer of higher density that contains the extracted inorganic salts, naphthenates and thio compounds.

- 15) A process as defined in claims 10, 11 and 12 in which both isolated layers can be removed for further processing.**
- 16) A process as defined in claim 10, 11, and 12 in which either liquid phase can be regenerated by azeotropic distillation.**
- 17) A process as defined in claim 13 in which the solvent in the lower layer or phase can be mechanically claimed by a Double Nip Thickener (DNT) and the sand or clays dried by azeotropic distillation of the remaining solvents.**
- 18) A process as defined in claim 2, which can be, executed at a lower temperature and hence requires less energy.**
- 19) A process as defined in claim 2, which can be executed with non-flammable solvent mixtures.**
- 20) A process as defined in claim 2 which can be used to hydrostatically transport solid ores at less than 0°C temperatures.**
- 21) A process as defined in claim 2 which eliminates toxic wastewater.**
- 22) A process as defined in claim 2 which eliminates the need for holding ponds.**
- 22) A process which provides a mechanism to separate the oils from mineral ores much closer to the mine site because of the reduced size of the required processing equipment.**
- 23) A process which, on a small scale, can be mounted on a transportation vehicle and which, in the case of oil spillage and contamination of the land could be used to rejuvenate said land. An example would be sand on beaches that have become oil laden because of oil spillage disasters on the high seas.**

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